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AEC Research and Development Report

Mathematics and Computing
July 1968

New York University

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NON-EMPIRICAL SCF-MO CALCULATIONS ON TRANSITION METAL COMPLEXES

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In this paper we shall demonstrate the feasibility of employing Gaussian functions as basis orbitals in molecular orbital computations on transition metal complexes. This calculation represents the first treatment of a transition metal complex ion involving all electrons and no approximations within the Roothaan SCF-MO formalism. The qualitative features of the calculation can be expected to have wide significance both for the understanding of the electronic structure of transition metal complexes and for the application of MO theory to large systems of this type.

We will report the results of calculations on the (hypothetical) square planar NiF_4^{2-} ion (the reasons for this particular choice will be explained later) and discuss those interesting ground and excited state molecular electronic properties which can be extracted from a computed wave function.

It is well known that individual Gaussians are much poorer representations of atomic orbitals (AO's) than are single Slater type orbitals (STO's), especially in two very important areas: near the nucleus, and in the tail region of the AO. These deficiencies are very serious if one wants to use Gaussians as basis functions for molecular calculations. Of course, a single STO is also known to reproduce rather poorly the tail region of an AO, and it takes a linear combination of STO's to span adequately the whole space of an AO. This suggests the method whereby one can correct the deficiencies of the individual Gaussian type orbitals (GTO's); use many of them in linear combinations to form Gaussian type functions (GTF's) and then use the GTF's as the basis functions in the MO calculation. The proper linear combinations needed to form the GTF's are easily obtained either by directly fitting the Hartree-Fock AO's with GTO's, or doing an atomic analytic SCF calculation in a GTO basis. We find that on the average only 2 - 3 GTO's per STO are required for quantitatively comparable results.

This is illustrated in Figure I which compares the 3d AO of Ni^{2+} ($3d^8$ configuration) in the single Slater, Hartree-Fock, and Gaussian approximations. Note that the position of the maximum for the Hartree-Fock and GTF coincide and that they tail off pretty much together, in contrast to the single Slater function. The Gaussian curve is a linear combination of 5 GTO's and is identical, on the scale of this figure, with the 2 term Slater representation computed by J.W. Richardson.(2)

This ratio of 2-3 Gaussians per Slater means that we must use a basis set 2-3 times larger for comparable results and evaluate many more integrals. Fortunately, the speed with which the necessary two-electron integrals over GTO's can be computed more than compensates for the handicap of the larger basis. This very favorable speed is due entirely to the fact that all the multicenter integrals over GTO's can be evaluated using simple analytic formulas which are easily coded in FORTRAN language, without recourse to complex numerical integration techniques, numerous slowly convergent expansions, or sophisticated programming structure.(3) This is the fundamental reason for using Gaussians.

To summarize, the MO wave function is an anti-symmetrized product of MO's which are expressed as linear combinations of GTF's. The coefficients of the GTF's in the MO's are determined variationally via the well-known Roothaan Hartree-Fock equations.(4) The GTF's are themselves linear combinations of GTO's but with the coefficients in these linear combinations fixed either directly or indirectly by previous atomic SCF calculation. Finally, and this is to be emphasized, no loss in accuracy in the computed MO's is necessary using Gaussians as basis functions provided that they are used properly, in the sense that a sufficient number of them are used to span adequately the function space.

The transition metal ion complex whose ground state wave function we have computed is the 66 electron NiF_4^{2-} ion in a square planar geometry. Actually, this ion has not been observed in a planar configuration. However, the planar $PdCl_4^{2-}$ complex ion is well known and has been very extensively studied.(5) Making reasonable extrapolations from the known shifts in behavior in going from Ni(II) to Pd(II) and F^- to Cl^- it was hoped to obtain reasonable good estimates of properties to compare with those computed here for NiF_4^{2-}. Unfortunately, this expectation was not realized in a quantitative manner.

Outside of a specific interest in the square planar situation, the reasons this particular ion was chosen for our initial study are three-fold. Square planar Ni(II) complexes are predicted to be closed shell in the ground state. This avoids the conceptual and practical difficulties that are known to arise in rigorously applying the SCF method to open shell electronic configurations. Further, since the D_{4h} symmetry has only 2 doubly-degenerate representations, it is likely that the excited electronic states calculated in the virtual orbital approximation would not involve the separation of multiplet states arising from electrons distributed in two partially occupied, multiply degenerate MO's. Finally, square planar

$NiF_4{}^{2-}$ is planned to be part of a series of calculations on Ni(II)-F complexes which will include $NiF_4{}^{2-}$ (tetrahedral), NiF_2 (linear), and $NiF_6{}^{4-}$ (octahedral).

The coordinate system used in the calculation has the nickel atom at the origin and the four fluorine atoms in the xy-plane. A Ni-F bond length of 2.00 Å was assumed.

The basis set for the square planar $NiF_4{}^{2-}$ calculation is given in Table I which shows the distribution of both the GTF's and GTO's in the basis set with respect to the AO's on Ni and F. Notice that some of the AO's are represented by two basis functions. Especially important are the 3d on Ni and 2p of F. This double zeta representation allows sufficient freedom so that the free ion AO's may adjust to the molecular environment in the course of the SCF calculation. For example, the five term Gaussian representation of the Ni^{2+} 3d AO was split up into a long range and a short range component. This allows the 3d AO either to expand or contract; i.e. it allows the energetics of the calculation to determine the spatial extension of the 3d AO in the complex. An analogous argument applies to the F^- 2p which is represented here by 2p and 2p' basis functions.

The resultant ground state ordering and orbital energies of the computed MO's are shown in Figure II. We would hasten to point out that all previous notions of the MO orderings in the diamagnetic square planar complexes of necessity arose from absorption spectra measurements, whether optical or magneto-optical. Unfortunately, absorption spectra involve both a ground state and an excited state, and evidence is here presented that the energy ordering of the ground state MO's does not necessarily determine the energy ordering of the excited states, and vice-versa. We will return to this after a closer look at the ground state.

The calculation shows the electronic structure built up starting with the "core" electrons; 1s, 2s, 3s, 2p, 3p on Ni and 1s, 2s, on F. The valence shell begins with the 3d orbital MO's, so called because Mulliken population analysis(6) shows them to be predominantly metal 3d. Then come all 24 F^- 2p electrons sandwiched within a narrow range of 6,000 cm^{-1}. This completes the occupied levels. The first unoccupied MO is the Ni 4s, then the $3d_{x^2-y^2}$, and the 4p last.

The population analysis shows that the MO's are rather completely segregated between the Ni and F orbitals, except for the $6a_{1g}(3d_{z^2})$ MO which has a substantial amount of F 2p character. Note also that z^2 is the highest occupied 3d orbital and that xy is lowest. From the orbital energy diagram presented here we would expect the first electronic transition to be F 2p to Ni 4s, but in fact, as we will show, this expectation is not fulfilled: Although the orbital energy gap between occupied and unoccupied d-orbital MO's is over 190,000 cm^{-1}, the d - d bands are calculated to fall lowest, in the visible and near UV regions of the spectrum.

The total orbital populations in this computation are: Ni $(core)^{18.00} 3d^{8.13} 4s^{0.20} 4p^{0.49}$ and F $(core)^{3.96} 2p^{5.84}$. The point of interest here is that the total occupancy of the Ni 3d orbitals is almost identical with the free ion configuration, $3d^8$. However, the 4s and 4p orbitals draw electrons from the ligands so that the computed net charge of +1.12 on the Ni is substantially reduced from the formal ionic value of +2, while each F has a computed net charge of -0.78.

The computed MO's can be interpreted to give two types of information. The first is covalency, which is the extent of mixing or interaction of the ligand and metal AO's and is reflected in the relative weights of metal and ligand coefficients in the computed MO's. The second type of information is the distortion of the basis set AO's themselves; i.e. the change in the spatial extension of an AO in the complex when compared to its spatial extension in the free atom or ion. It is unfortunate that heretofore all discrepancies in the properties computed assuming the 3d radial function of the free ion to be a valid representation of the 3d AO in the complex have been attributed entirely either to expansion (or contraction) of the free ion AO, which is the crystal field view, or to covalency mixing, which is the traditional MO treatment of ESR, NMR, and optical data. In fact, both these mechanisms operate simultaneously and with the use of the double zeta representation we can examine the inherent expansion or contraction of AO's due to complex ion formation. This is illustrated in Table II.

The double zeta basis for the F^- 2p AO was obtained by breaking up a four term Gaussian representation into a long range and a short range component. The expansion coefficients for atomic F^0 and the F^- ion using the same set of exponents are given in the first two columns and beneath them is the ratio in various MO's. C_4 is the coefficient of the Gaussian with the smallest exponent so that a smaller ratio means a more diffuse orbital. Note that the ratios for F^0 and F^- differ by about 30%.

The corresponding coefficients in two ligand 2p MO's are shown; the π non-bonding $1b_{2u}$, and the sigma bonding $7a_{1g}$. The ratio of C_3/C_4 for both these MO's is extremely close to that found in the free F^- ion calculation.

An analagous result for the Ni^{2+} 3d AO is shown in Table III. Here a five term Gaussian expansion was broken up into a set of three and a set of two. Here we compare the ratio C_3/C_4 which does not depart significantly from that computed for the free metal ion in its formal +2 oxidation state, even for the $3d_{z2}$ MO which contains a significant amount of F^- 2p character. Note, however, that the orbital deformation, as reflected in the C_3/C_4 ratios is slightly different for each d-orbital MO. Thus, using a double zeta representation is equivalent to optimizing the spatial extension of the basis function separately for each computed MO.

The excited electronic states of the $NiF_4{}^{2-}$ ion are presented in Table IV. The qualitative features of the computed absorption energies are quite clear. The ordering of the states arising from d-d transitions in the virtual orbital approximation gives those originating from xy, and xz, yz low in energy and that from z^2 high in energy, quite the opposite from that expected from the one electron orbital energies in the ground state. The triplets are very low-lying, so low as to fall in the near-IR region of the spectrum.

Since the xy, xz, yz, and x^2-y^2 MO's are overwhelmingly of metal character we would expect that in going from NiF_4^{2-} to $PdCl_4^{2-}$ only the Ni to Pd shift should matter, giving a slight blue shift in the computed energies of these transitions. On the other hand, transitions originating from the z^2 MO, which contains 23% F^- 2p, and considering the tremendous blue shift effect of the F^- ion, should be red shifted in going to $PdCl_4^{2-}$. Thus, the d-d bands in $PdCl_4^{2-}$ should be found in the 10-36,000 cm^{-1} range with the singlet $z^2 \rightarrow x^2-y^2$ transition highest in energy. These conclusions are not inconsistent with the observed absorption spectrum of $PdCl_4^{2-}$, with the d-d bands reported in the range 17-30,000 cm^{-1}(5). However, a more detailed assignment of the d-d states of $PdCl_4^{2-}$ in light of a calculation on NiF_4^{2-} would probably tax the powers of the calculation beyond its present capabilities.

Two high intensity bands have also been observed in the absorption spectrum of the $PdCl_4^{2-}$ ion at 36,000 and 45,000 cm^{-1}, with oscillator strengths estimated at about .2 and .5, respectively. Anex(7) has measured the polarizations of these bands and finds them both to be xy or in-plane polarized, with a weak z polarized band hiding under the higher energy xy polarized band.

The lowest energy symmetry allowed transitions calculated for NiF_4^{2-} are shown in Table V together with their oscillator strengths as computed from the dipole velocity and dipole length. These excited states are, of course, computed to fall at very high energy in NiF_4^{2-} due to the tremendous blue shift effect of F^-. But most surprising , the assignments of the lowest-lying of these transitions are all 2p-4s rather than the usually assumed 2p-3d. The relative orderings and intensities of the three computed 2p-4s bands are consistent with the observations of Anex, although the same can be said about the three 2p-3d bands which are next highest in energy. The use of an unoptimized single zeta representation for the Ni 4s orbital renders any conclusions about these assignments tentative.

In Table VI we give a detailed breakdown of the computation of the excitation energies. The equation is given at the top and the values of the contributing terms for the three single d-d transitions and the lowest-lying charge transfer transition are given in their respective columns. e_i and e_j are the orbital energies, J_{ij} and K_{ij} are the Coulomb and Exchange integrals, respectively.

The importance of the electron repulsion correction of the Coulomb integral to the simple differences of ground state orbital energies is immediately obvious. Note that for the d-d bands the Coulomb integral is very similar to that calculated from the free ion metal 3d orbitals alone, given in parentheses next to the MO values. In contrast note the small Coulomb integral value for the 2p-4s transition. Thus although the orbital energy differences for the d-d transitions are considerably larger than those for the charge transfer bands, the enormous release in energy obtained by splitting up a pair of d orbital electrons more than compensates for this large difference; i.e. the enormous self-repulsion of the 3d electrons must be considered as a crucial factor in the gross ordering of the low-lying excited state configurations.

The ratio of the Coulomb integral for the $z^2 \rightarrow x^2-y^2$ transition in the molecule to its free ion value is much smaller than for the other d-d transitions. This is a direct outcome of the admixture of F^- 2p orbitals in the z^2 MO. Thus, although the orbital energy difference is smallest for the $z^2 \rightarrow x^2-y^2$ excitation, reflecting the high energy of the z^2 MO, the value for the Coulomb integral due to covalent mixing gives an excitation energy for $z^2 \rightarrow x^2-y^2$ highest of all the d-d transitions. Thus the amount of covalent mixing and the accompanying variable reduction in the electron repulsion integrals apparently determine the finer details of the ordering of the excited states in NiF_4^{2-}.

The purpose of this computation has been to demonstrate to those interested in the application of MO theory to problems in inorganic chemistry the feasibility of doing non-empirical SCF-MO calculations on transition metal complexes with Gaussian type basis functions. The specific example discussed, square planar NiF_4^{2-}, although admittedly a hypothetical complex, was chosen as a prototype to illustrate certain general characteristics of the calculation. Since the presentation of these results, we have redone the computations using completely optimized atomic wavefunctions for both the Ni^{2+} and F^- ions. The results are in qualitative agreement with those reported above. In addition, SCF calculations have been completed on octahedral NiF_6^{4-} as part of a study of the interesting spin properties of this species which give rise to transferred hyperfine interactions, spin-orbit coupling, and electronic g-factors.

Acknowledgement

The authors would like to thank Dr. D. Neumann for many helpful discussions and programming assistance. This research was supported in part by the National Science Foundation under grant GP-5677.

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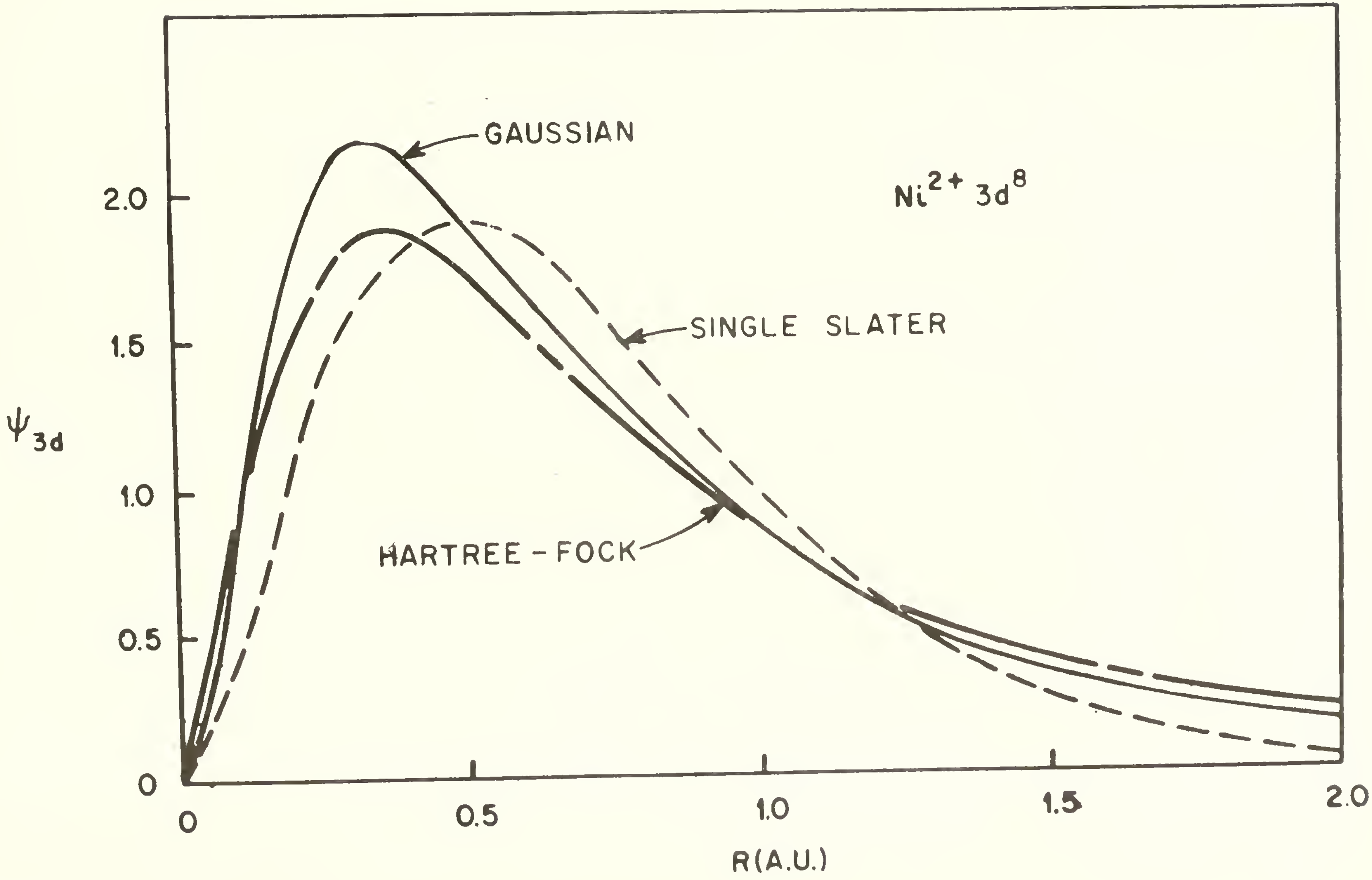

Figure II 3d wave function of Ni^{2+} ($3d^8$ configuration) in the single Slater, Hartree-Fock, and Gaussian approximation

Figure II GROUND STATE OF NiF_4^{2-} (D_{4h})

% Minority Composition		% Majority Composition			Orbital Energy (cm^{-1})
4.2	2p	95.8	$4p_z$		+141,040
7.3	2p	92.7	$3d_{x^2-y^2}$		+139,980
8.5	2p	90.1	4s		+114,790
			2p	24 electrons	- 17,790 - 23,360
22.9	2p	77.1	$3d_{z^2}$		- 46,530
5.7	2p	94.3	$3d_{xz,yz}$		- 50,370
4.4	2p	95.6	$3d_{xy}$		- 67,390
			Core	34 electrons	

Table I BASIS SET FOR NiF_4^{2-}

		GTF's	GTO's
Ni^{2+}	1s, 1s′, 2s, 2s′, 3s, 4s	6	12
	2p, 2p′, 3p, 4p	12	24
	3d, 3d′	12	30
F^{-}	1s, 2s	2	7
	2p, 2p′	6	12
		62	144

Table II EXPANSION AND CONTRACTION OF FLUORINE AO's

	atomic (F^-)	atomic (F^0)	$1b_{2u}(\pi^{n.b.})$	$7a_{1g}(\sigma^b)$
C_1	.02652	.02905		
C_2	.17158	.18408		
C_3	.43180	.49025	.44212	.35716
C_4	.60428	.53497	.59240	.51830
C_3/C_4	.715	.916	.746	.689

Table III EXPANSION AND CONTRACTION OF NICKEL AO's

	atomic (Ni^{2+})	xy	z^2	xz,yz
C_1	.07302			
C_2	.23864			
C_3	.45326	.44236	.38260	.43072
C_4	.40293	.39003	.35841	.39801
C_5	.17167			
C_3/C_4	1.125	1.134	1.067	1.082

Table IV ELECTRONIC STATES OF NiF_4^{2-}

One Electron Transition	State	Energy (1000 cm^{-1})	$PdCl_4^{2-}$ (ϵ_{max})	$PtCl_4^{2-}$ (ϵ_{max})
	$^1A_{1g}$	0		
$xz,yz \rightarrow x^2-y^2$	^3E_g	4.0	?	18.0 (2)
$xy \rightarrow x^2-y^2$	$^3A_{2g}$	11.0	?	20.7 (2)
$xz,yz \rightarrow x^2-y^2$	^1E_g	19.0	22.8 (104)	29.5 (46)
$xy \rightarrow x^2-y^2$	$^1A_{2g}$	19.5	20.0 (67)	26.3 (28)
$z^2 \rightarrow x^2-y^2$	$^3B_{1g}$	26.0	17.5 (13)	24.0 (5)
$z^2 \rightarrow x^2-y^2$	$^1B_{1g}$	40.0	29.5 (67)	36.5

Table V CHARGE TRANSFER STATES OF NiF_4^{2-}

One Electron Transition	State	Energy (cm^{-1})	f(∇)	f(r)
2p → 4s	$^1E_u(x,y)$	69,400	.055	.045
2p → 4s	$^1E_u(x,y)$	86,200	.491	.263
2p → 4s	$^1A_{2u}(z)$	91,400	.195	.106
2p → 3d	$^1E_u(x,y)$	100,100	.081	.212
2p → 3d	$^1A_{2u}(z)$	101,600	.000	.000
2p → 3d	$^1E_u(x,y)$	107,000	.165	.285
3d → 4p	$^1A_{2u}(z)$	108,000	.209	.270

Table VI EXCITATION ENERGIES OF NiF_4^{2-}

$${}^1E\ (i \rightarrow j) = \varepsilon_j - \varepsilon_i - J_{ij} + 2K_{ij}$$

1 a.u. = 219,450 cm^{-1}

Transition	$\varepsilon_j-\varepsilon_i$(a.u.)	J_{ij}(a.u.)	K_{ij}(a.u.)	Energy(cm^{-1})
xz,yz → x^2-y^2	.86741	.84913(.95806)$^{(a)}$	.03455	19,200
xy → x^2-y^2	.94495	.89496(.99429)$^{(a)}$	.01940	19,500
z^2 → x^2-y^2	.84991	.73132(.94598)$^{(a)}$	.03264	40,300
2p → 4s	.54432	.22783	.00738	69,400

(a) Computed from free ion 3d functions.

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